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(54) Abstract Title: **Attachment of a patterned array of porous ceramic material to a substrate**

(57) A patterned array of porous ceramic material 11, capable of holding a chemical material, is screen printed onto substrate 12. Also disclosed is the placing of a patterned array of porous ceramic material 21, capable of holding a chemical material, into holes within a substrate 22. Further disclosed is the attachment of a patterned array of porous ceramic material (32, fig.3B), capable of holding a chemical material, to a substrate (31, fig 3B) via photolithographic patterning. The porous ceramic materials 11,21,(31,fig.3B) in each case are sintered to solidify, and thus provide a patterned array of material capable of immobilising and isolating chemical species for analysis.

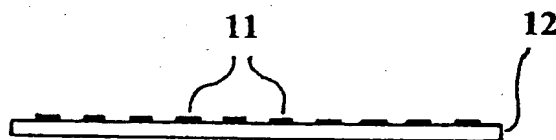


Figure 1B



Figure 2C

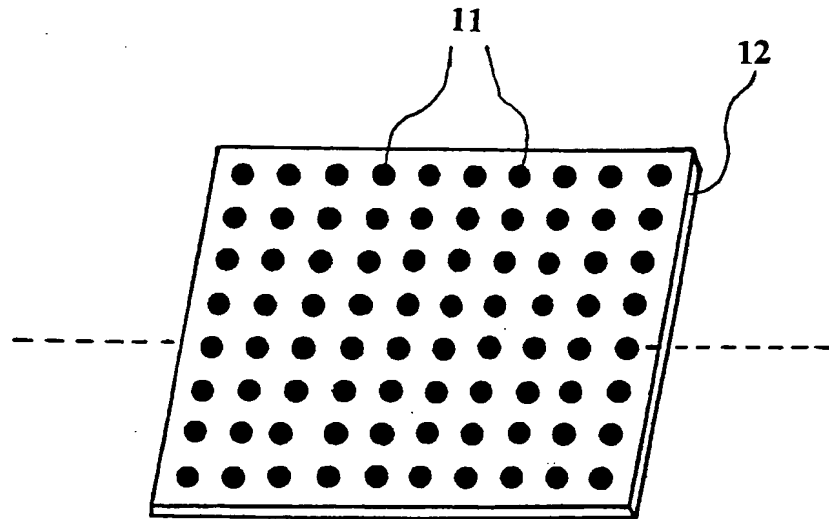


Figure 1A

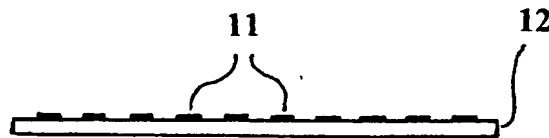


Figure 1B

Figure 1

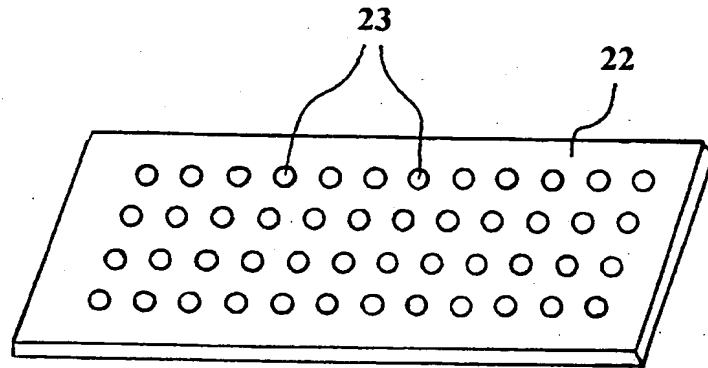


Figure 2A

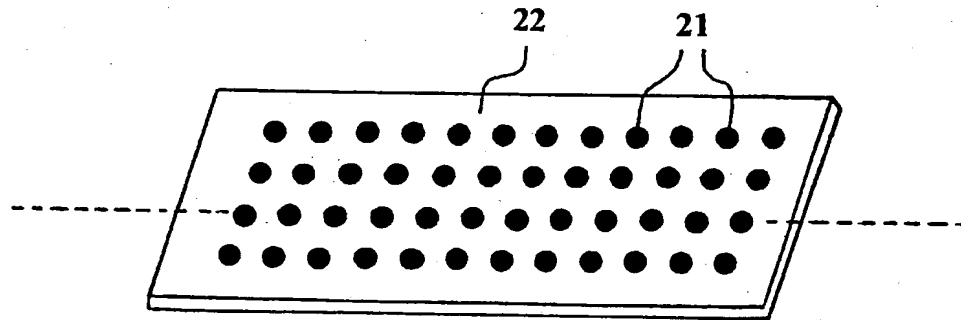


Figure 2B

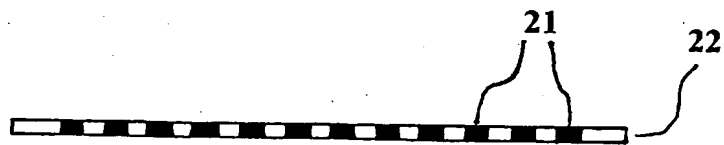


Figure 2C

Figure 2

Figure 3

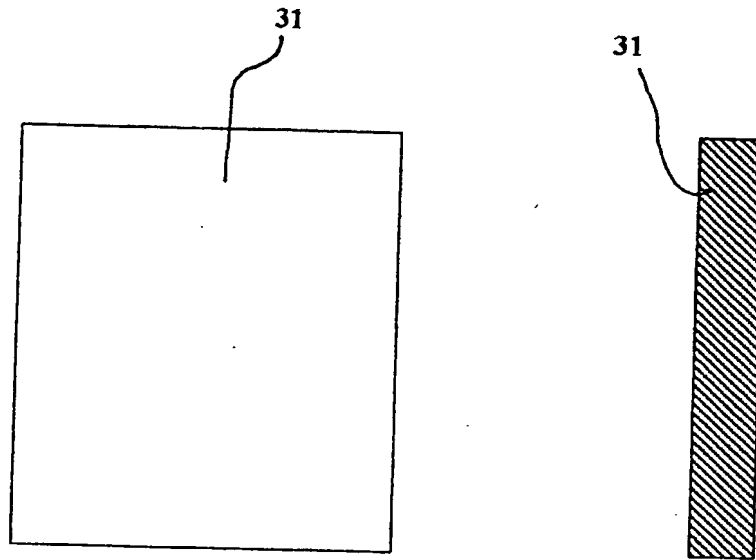


Figure 3A

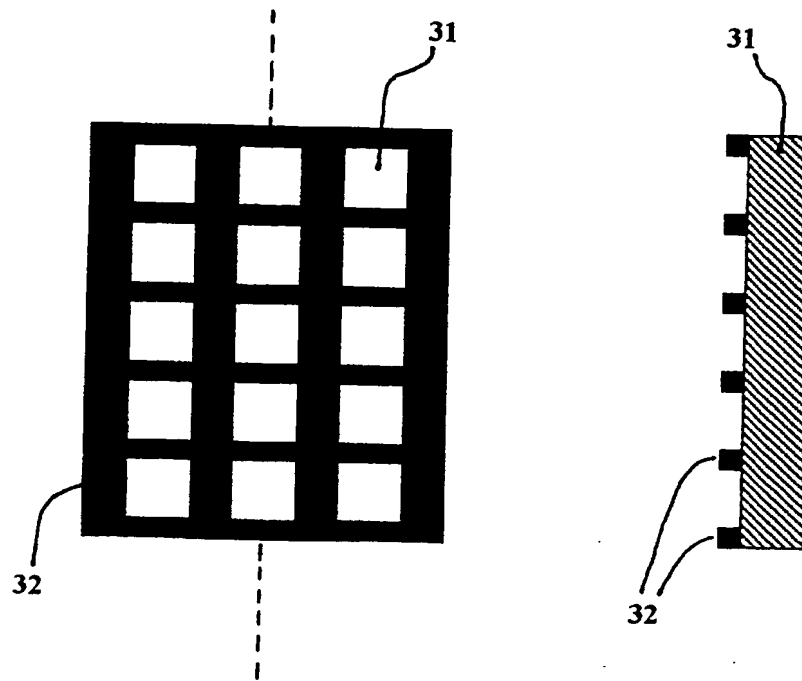


Figure 3B

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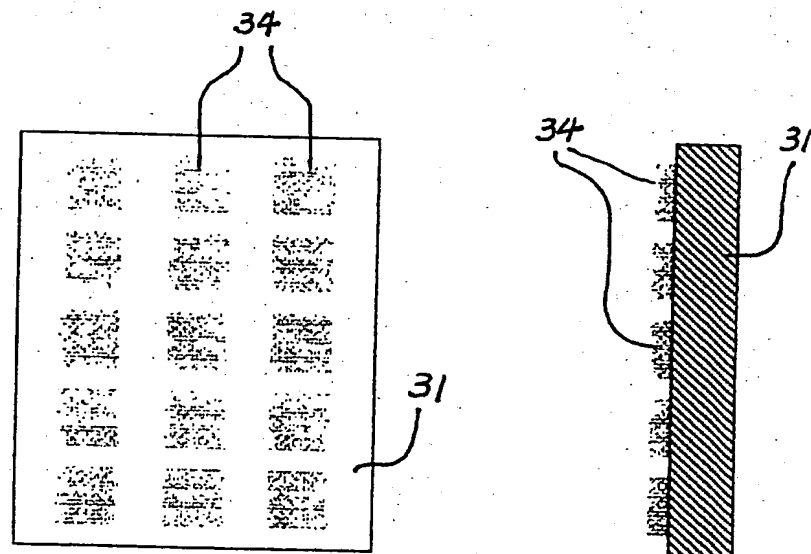
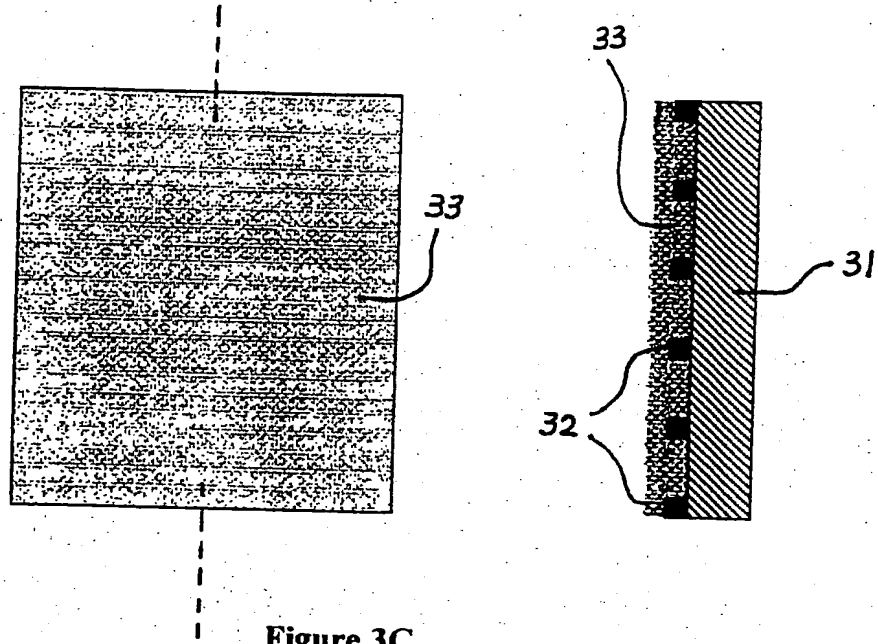


Figure 3D

Figure 3-

POROUS CERAMIC PATTERNED SUBSTRATES

TECHNICAL FIELD:

This invention relates to manufacturing and designs of non-metallic oxide substrates on or in which patterns of porous ceramic media are formed. Extremely large number of fine pores in the ceramic media can be used to store or isolate chemical species in a more secured fashion. The high porosity of the pervious ceramic media provides substantially increased surface areas that have the advantage of enhancing expression signals of chemicals immobilised in them.

BACKGROUND:

Since the emergence of the first DNA chip some years ago, the technology has become more matured, especially in medical diagnosis applications. At the same time there have been rapid developments of various bio- and chemical devices employing similar technical disciplines, such as biosensors, bioinformatics and chemical sensors.

In virtually any of these developments, a key aspect of the technology is to immobilise or isolate a larger number of chemical species on a substrate. This miniature plate containing large number of chemical species is often referred as chemical-chip. The substrate materials are fabricated from plastics, glass slides and etched silicon wafers. A common feature for these array substrates is that the chemical species are only deposited onto the impervious two-dimensional surface and tethered to the substrates through inter-surface bonding.

A common method of chemical array preparation is to deposit tiny volumes of chemical species in liquid form to the pre-designated sites (e.g. a free surface or small previously formed wells) on a substrate surface. By accurately controlling the volume of the chemical liquid and injection characteristics, good chemical arrays are produced. However, with so many types of chemical compounds, their properties such as viscosity and surface tension (or free surface energy between the compound and substrate) vary greatly. This means that even with exactly the same injected volume, the spot sizes (of circular shape) of a chemical array can not be the same (e.g. same volumes of water and oil on a glass slide). This problem becomes more serious when trying to form a high density chemical array on a free surface substrate, as profusion of the injection is more likely to occur that may result in distortion and mix up of the isolated array elements. Consequently, the quality (one of the important requirements is the perfect visual appearance of the array) and the reproducibility of a chemical array often become difficult to maintain.

Another drawback for the inter-surface bonding between a chemical species and an impervious substrate (whether it is made of a glass, plastic or silicon wafer) is that chemicals have different adhesions (or bonding capability) on an impervious surface of a particular material. For this reason, while some chemicals can be well attached to a substrate surface, others may be not. The consequences are that the difficulty of manufacturing high-density chemical arrays occurs and reliability of such high-density chemical arrays is reduced.

Therefore there is a need for improved substrate materials that allow various chemical compounds in liquid form to be more conveniently and reliably attached onto. Moreover, the attached chemicals are more firmly tethered to the pre-designated regions, thus making it more robust for applications in various environments.

For almost all applications of chemical arrays, the chemical species immobilised in the array are expressed optically, electronically or/and magnetically. As a single array element occupies a very small area (e.g. for 2,500 arrays per one centimetre square, the array element spot area is typically 0.01 mm^2), the expression signal (whether it is optical, electrical or magnetic) generated from such a small spot is weak for reliable detection and analysis. This results in serious drawbacks for practical applications, as the detection and analysis technology for the chemical arrays needs to be largely unconventional (hence high cost). Therefore there is also a need for substrates that can substantially increase the surface area within each array element.

SUMMARY OF PRESENT INVENTION:

Accordingly the present invention overcomes the above-mentioned problems and disadvantages associated with the substrates that have impervious surfaces and provides manufacturing methods for glass and ceramic substrates on or in which patterns of porous ceramic media are formed.

The invention describes processing methods for forming patterns of porous ceramic media on the surfaces of glass and impervious ceramic supporting plates by screen-printing and photolithographic patterning-wet ceramic coating. The invention also provides a method of making porous ceramic array in a supporting plate by filling a wet ceramic in the arrayed through holes previously machined in the impervious ceramic or glass supporting plate.

The invention described herein includes compositions of ceramic pastes and suspensions suitable for the mentioned processing methods.

In another aspect, the invention relates to the wet ceramic compositions and the procedures of preparing these compositions that have good adhesion on the surfaces of glass and dense ceramics (e.g. impervious alumina ceramic) and produce porous ceramics on sintering. This adhesion is retained after wet processing (e.g. screen-printing), drying at temperature between $25\text{-}100^\circ\text{C}$ and sintering between $300\text{-}1000^\circ\text{C}$. In this invention, the patterns of porous ceramics formed on or in glass plates are sintered between $300\text{--}600^\circ\text{C}$ and the patterns of porous ceramics formed on or in impervious ceramics plates are sintered between $500\text{-}1000^\circ\text{C}$.

In still another aspect, the pervious ceramic arrays processed with the methods herein described have various pore size ranges after sintering at elevated temperatures. By varying particle sizes of a constituent in composition, different pore size range within a pervious ceramic is achieved. Closely related to this aspect is that the processing feature and good adhesion on the supporting plate surfaces are not affected by such variations.

As broadly described herein, the present invention enables a customised array or pattern of porous ceramic media on or in a small glass plate or ceramic plate to be manufactured. Such a miniature plate containing porous ceramic array may have following features and advantages

1. The array elements are made of a ceramic media that contains large number of interconnected micro-pores. When a chemical in liquid form is deposit (e.g. by injection) onto such an array, it is drained continuously into this array element by capillary force and spreads uniformly into the whole shape of this array element. This will stop the profusion of the deposited chemicals and thus prevent the mix up of the chemicals.
2. The chemical species are stored or isolated more securely in the interconnected porous structure within the array elements, making it more robust for applications where

chemical species need to be tightly tethered or immobilised onto a substrate. It is virtually not possible to wipe away the chemicals immobilised in the porous arrays prepared in this invention. As a comparison, similar chemicals deposited on a flat impervious surface (e.g. glass or plastic) are easily wiped off. In this aspect, the porous array substrates prepared in this invention are more likely to be adopted in applications where a number of different chemicals are stored or isolated on a single miniature plate.

Furthermore, when the pore sizes of the porous arrays are very small, for example, in the range 10-100 nanometers (10^{-9} metres), the chemical species are very tightly locked in these pores. In such nano-porous arrays, the immobilised chemical species can be subject to treatments and reactions in liquid media, because they are not easily washed out from the porous arrays.

3 In this invention, the porous ceramic media formed on or in a supporting plate have pore sizes in a narrower region within the range between 10-1000 nanometers (10^{-9} metres). As a result, the surface area within a single array element is substantially higher than the area this very array element occupies on the substrate. This allows substantially more chemical to be attached or stored within a array element, producing an increased density of the chemical molecules as compared to the array elements merely formed on a two dimension plate surface (e.g. on a glass slide surface). In practical applications, an increased chemical density will enhance the intensity of a signal to be detected whether it is optical (e.g. florescence), electrical or chemical. Practically this means that the appliance where the chemical arrays are used may be made more reliable with the porous ceramic array substrates as provided in this invention.

DESCRIPTION OF THE DRAWINGS

Figure 1

Figure 1A and 1B are collectively referred to as the Figure 1.

Figure 1A is a perspective view of a porous ceramic array substrate. Figure 1B is a cross-section view through this porous ceramic array substrate. Neither figure is to scale.

An embodiment of the present invention in Figure 1A consists of a rectangular plate 12 and dot porous ceramic array 11 attached to the surface of this plate 12. The base plate 12 is made of either glass or an impervious ceramic, such as non-porous alumina. The thickness of the plate 12 may be between 0.25 – 2 mm. The dot porous ceramic array 11 is a series of porous ceramic dots (a porous ceramic dot is also referred to as a porous array element) formed on the surface of the plate 12. These dots 11 are essentially porous ceramic media attached on the impervious surface of the plate 12 by screen printing or coating after photolithography patterning of the plate 12. The sizes (diameters) of the porous array elements processed by screen-printing may be in the range between 0.05-1.5 mm. The sizes (diameters) of the porous array elements processed by coating after photolithography patterning may be in the range between 0.01-1.5 mm.

Figure 1B schematically illustrates the cross-sectional view of the embodiment.

Although the shape of the porous ceramic dots 11 in Figure 1A is circular, other shapes such as rectangular and oval are easily formed in the same way. The base plate 12 as indicated in Figure 1A may also be in other shapes such as circular.

Figure 2

Figure 2A, 2B and 2C are collectively referred to as Figure 2.

Another embodiment of the present invention in Figure 2A consists of a rectangular impervious base plate 22 on which arrays of small through holes (or through channels) 23 are formed. These holes are then filled with porous ceramic media to form arrays of

porous ceramics as indicated at 21 in Figure 2B. Figure 2C schematically illustrates the cross-sectional view of the embodiment.

The base plate 22 is made of either glass or impervious ceramic materials (e.g. alumina). The thickness of this base plate may be in the range of 0.25-2 mm. The array of through holes (23 as indicated in Figure 2A) are drilled by mechanical means, high-pressure water-jet, photosensitive/etching method or laser. These holes may have diameter in the range between 0.05 – 1 mm. The shape and the size of the through holes 23 can be made in accordance to a specific requirement.

As illustrated in Figure 2B, the array of holes pre-formed in the impervious base plate 22 are filled with porous ceramics. The array of porous ceramic filled holes now become array of porous/impervious ceramic 21. Each of the array elements is an isolated pervious medium that can contain or immobilise a single chemical. The dimension of such porous ceramic array determines the number of chemical species that can be immobilised or isolated on the substrate.

Figure 3

Figure 3A, 3B, 3C and 3D are collectively referred to as Figure 3.

Figure 3 illustrates the procedure for preparing porous ceramic patterned substrates by a method where wet ceramic coating is combined with photolithography.

Figure 3A shows a base plate 31 made of glass (e.g. normal microscope glass slide) or an impervious ceramic (e.g. alumina plate). It is used as a support substrate.

Figure 3B shows the plate on which an array pattern is formed by photolithography method. The pattern of the Photoresist masking film 32 is obtained after coating the base plate 31 with a positive Photoresist polymer, exposing it through UV radiation with a patterned mask and treatment in a developing solution. The squares in Figure 3B have original surface of base plate 31.

Figure 3C shows the photolithographically patterned plate of which the overall surface is coated with a wet ceramic paste, a suspension or a solution (the compositions and preparation procedure for these are described in other parts in this invention). This coated layer is indicated by 33.

Figure 3D shows the porous ceramic array 34 attached to the surface of the base plate 31 after acetone immersion treatment and/or sintering at an elevated temperature (e.g. 560 °C).

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the purposes as described earlier herein, the present invention comprises the compositions of wet ceramics that can be attached onto the surfaces, or embedded into the bodies, of glass and impervious ceramic supporting plates, processing methods and designs of porous/pervious ceramic array substrates.

The arrays of three dimensional porous ceramic spots (or patterns) are attached to the surfaces of glass or impervious ceramic supporting plates by the method of wet ceramic screen-printing, followed by sintering of such array plates.

A combined method of photolithographic patterning and wet ceramic coating to produce patterns and arrays of pervious ceramic media is herein described in detail. The steps of this method are schematically illustrated in Figure 3. A surface of a glass or an impervious ceramic plate is coated with a positive Photoresist (e.g. SP22-1NH or Sp2029, Shipley Inc, UK). The coated surface is then exposed to ultra-violet radiation through a special mask with a required pattern. Next this plate is immersed in a developing solution (normally sodium hydroxide solution) during which the sections (or parts) of the

Photoresist that has been exposed to UV radiation is removed. The Photoresist coating layer on the section (or parts) that has not undergone UV radiation remains on the surface of the glass plate, this layer will provide a mask to prevent a direct contact (or sticking) of porous ceramic to be coated in the next step with the base plate. Thus obtained plate is referred to as a photolithographically patterned plate (Figure 3B). Next the overall surface of the photolithographically patterned plate is coated with a wet ceramic paste or ceramic suspension or a ceramic colloidal solution by dip-in coating or screen-printing or means of doctor blade. Figure 3C schematically illustrates thus coated plates. In next step, the sections (or parts) covered with the both Photoresist (between the base plate and ceramic coating layer) and wet porous ceramic coating (on the top of Photoresist layer) are dried between 40-80 °C for up to 60 minutes during which the wet ceramic layer is solidified. The thoroughly dried plate is then treated by immersing it in acetone to dissolve the Photoresist, and at the same time, to detach (or peel off) the porous ceramic coating positioned on the top of the Photoresist film. It is also possible, without treating the wet ceramic coated plate in acetone, to burn off the Photoresist film to detach porous ceramic coating positioned on the top of it during the final sintering step. In the final step, the plate prepared through the steps described above is sintered at an elevated temperature between 350 –1000 °C. When the base plate (as illustrated in Figure 3A) is made of a glass, sintering temperature is between 350-600 °C. When the base plate is made of an impervious ceramic (e.g. alumina), sintering temperature is between 500-1000 °C. The finally obtained plate with a porous ceramic pattern attached to its surface is schematically illustrated in Figure 3D

The invention also provides a method of making a substrate containing an array of through holes that are filled with a porous ceramic medium. In this method, a array of through holes are first machined by means of laser, mechanical drilling or photosensitive etching in a base plate made of glass or impervious ceramic materials such as alumina and photosensitive glass-ceramics. Then the through holes in the array are filled with a specially formulated wet ceramic paste as described in other parts of this invention. Next the wet ceramic filled substrate is dried between 40-80 °C and sintered at a temperature in the range between 350 and 1000 °C. This method is schematically illustrated in the accompanying Figure 2.

For convenience of description, the term “wet ceramics” as used herein refers to printable pastes, ceramic colloidal solutions and ceramic powder suspensions. These printable paste, ceramic colloidal solutions and ceramic powder suspensions will be converted into porous ceramics after being dried and sintered at elevated temperatures.

A wet ceramic is prepared by mixing thoroughly a liquid ceramic carrier with one or more metal oxide powders such as alumina and silica. A good mixing of a liquid ceramic carrier with one or more metal oxides is achieved by blade-agitation in a container, grinding with mortar and pestle, or ceramic ball milling in a closed ceramic jar. In some cases the pastes are further mixed by roller-mills.

According to the present invention, three liquid ceramic carriers (A, B And C) having following composition ranges are used to form wet ceramics:

Liquid Ceramics Carrier A:

It was established in the invention that $(C_2H_5)_4Si$ (Tetraethyl Silicate), when combined with water and Ethanol/methanol, formed a good ceramic carrier solution for binding ceramic powders. The composition range of such solution may be (percentage by weight):

$(C_2H_5)_4Si$ (Tetraethyl Silicate): 10-50%

Methanol or/and ethanol: 20-70%
 10% H_3PO_4 aqueous solution: 0-10%
 10% HCl or/and 10% HNO_3 aqueous solution: 0-10%
 The balance (to 100%) consists of only pure water.

When thoroughly stirred at room temperature, above mixtures form clear solutions. Such solutions yield solid SiO_2 and P_2O_5 when dried and heated to high temperatures (300-1000°C).

Liquid Ceramic Carrier B:

The following composition range is in weight percent:

Colloidal silica (e.g. Du Pont Syton X30, W30, W50 and Ludox grades): 5% – 30%
 Boric Oxide (B_2O_3): 0%-8%
 10% H_3PO_4 aqueous solution 0.2-10%
 The balance to 100% (by weight) consists of only water.

Liquid Ceramic Carrier C:

The following composition range is in weight percentage:

Zirconyl Chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$): 2.5-40%
 Colloidal silica (e.g. Syton X30, W30, W50): 0-15%

The balance to 100% (by weight) consists of only water.

According to the present invention, the metal oxides used in the preparation of wet ceramics are listed in the following table (Particle size ranges are in microns, or 10^{-6} metre):

Table 1

| Metal Oxide | Particle size range (1) | Particle size range (2) | Particle size range (3) |
|--------------------------|-------------------------|-------------------------|---|
| Al_2O_3 | 0 – 0.1 | 0 – 0.5 | 0 - 5 |
| $\text{Al}(\text{HO})_3$ | 0-0.1 | 0 - 1 | |
| SiO_2 | 0 – 0.05 | 0 – 0.1 | 0 – 0.5 |
| ZrO_2 | 0 – 0.1 | 0 – 0.5 | 0 - 1 |
| TiO_2 | 0 – 0.1 | 0 – 0.5 | 0 – 1 (5% Y_2O_3 stabilised) |
| BaTiO_3 | 0 – 0.5 | 0 – 1 | |
| ZnO | 0 – 0.5 | 0 - 1 | |

In order that the invention may be more clearly understood, some embodiments thereof are described, by way of example, with reference to the accompanying drawings

Liquid ceramic carriers used in the examples were:

A1:

12.4g $(\text{C}_2\text{H}_5)_4\text{Si}$ (Tetraethyl Silicate) was first mixed with 32.9g methanol. Then 0.5g 10% HCl (hydrochloride acid) aqueous solution, 2.2g 10% H_3PO_4 aqueous solution and 52.6g

water were gradually added in while the solution is continuous stirred. Such solution is further stirred for 30 minutes before ready for use.

A2:

34g (C₂H₅)₄Si (Tetraethyl Silicate) is first mixed with 31g methanol. Then 1.2g 10% HCl (hydrochloride acid) aqueous solution and 52.6g water were gradually added in while the solution was continuous stirred. Such solution was further stirred for 30 minutes before ready for use.

B1:

77.6g water, 20g 30% colloidal silica (Du Pont Syton X30), 4.2g 10% H₃PO₄ aqueous solution and 0.2g B₂O₃ were mixed by stirring continuously in a beaker for about 5 minutes. This solution was then ready for use as a liquid ceramic carrier.

B2:

65g water, 30g 30% colloidal silica (Du Pont Syton X30), and 7g 10% H₃PO₄ aqueous solution were mixed by stirring continuously in a beaker for about 5 minutes. This solution was then ready for use as a liquid ceramic carrier.

C1:

26g ZrOCl₂·8H₂O (Zirconyl Chloride) was dissolved in 64g water. Then 10g 30% colloidal silica (Du Pont Syton X30) was dispersed in the solution. Such mix was continuously stirred for 3 minutes. This solution was then ready for use as a liquid ceramic carrier.

C2:

19g ZrOCl₂·8H₂O (Zirconyl Chloride) was dissolved in 70g water. Then 11g 30% colloidal silica (Du Pont Syton X30) was dispersed in the solution. Such mix was continuously stirred for 3 minutes. This solution was then ready for use as a liquid ceramic carrier.

In following examples, the above described A1, A2, B1, B2 C1 and C2 are used as liquid ceramic carriers in the preparation of wet ceramics.

Example 1:

40g liquid ceramic carrier A1 is mixed with 66g alumina powder having particle sizes between 0 – 0.5 microns to form a smooth paste. This paste was screen-printable. When printed on a glass, dried in an oven (25-100 °C) and fired at 560 °C for 30 minutes, it formed a porous or pervious ceramic layer. Such a layer absorbed chemical solutions continuously.

An array 8x10 of circular spots of 1mm diameter, as schematically illustrated in Figure 1, was screen-printed with this paste on a glass plate of 1mm thickness. After drying at 60 °C for 20 minutes it was fired at 560 for 30 minutes. After cooling to room temperature, a glass plate with an 8x10 porous ceramic array on its surface was obtained. On this a plate, 80 different chemicals can be immobilised or isolated.

Example 2

Same as Example 1 except that the plate on which the paste (have same composition as described in Example 1) was printed was a 1 mm thick alumina plate.

Example 3

42g liquid ceramic carrier A1 is mixed with 5g fumed silica powder (Degussa) having particle sizes less than 0.1 microns to form a smooth paste. This paste is screen-printable.

An array of 20x60 circular spots of 0.4mm diameter with a distance of 0.6mm between spots was screen-printed with this paste on a normal microscope glass slide. After drying at 60 °C for 20 minutes it was fired at 540 °C for 30 minutes. After cooling to room temperature, a

glass slide with an array of 20x60 porous ceramic spots on its surface was obtained. On this a plate, 1200 different chemicals can be immobilised or isolated.

Example 4

50g $\text{Al}(\text{OH})_3$ (aluminium hydroxide) power having approximate particle sizes 0-1micron was mixed with 40g A1 liquid ceramic carrier to form a smooth, printable paste. Using this paste, an array 8x10 of circular spots of 1mm diameter, as schematically illustrated in Figure 1, was screen-printed on a 1mm thick glass plate. After drying at 60 °C for 20 minutes it was fired at 560 for 30 minutes. After cooling to room temperature, a glass plate with 8x10 porous ceramic array on its surface was obtained.

Example 5

43g liquid ceramic carrier A2 was mixed with 4.5g titanium oxide powder having particle sizes finer than 0.1 microns (Degussa, P25 TiO_2 powder) to form a thin but smooth paste. This paste was used to apply very thin coatings on the glass plates using the screen printing method.

A 20x60 array of circular spots of 0.4mm diameter was screen printed with this paste on a normal microscope glass slide. After drying at 40 °C for 60 minutes in an electric furnace, the temperature was raised at the rate of 3 degree per minute to 540 °C where it was held for 30 minutes. After cooling at a rate of 5 degree per minute to room temperature, a glass slide with an array of 20x60 porous ceramic spots attached to its surface was obtained. On this a plate, 1200 different chemicals may be immobilised or isolated.

Example 6

40g liquid ceramic carrier A2 was mixed with 23g aluminium oxide powder having particle sizes less than 5 microns and 2g aluminium oxide powder having particle sizes less than 0.1 microns (Degussa aluminium oxide C) to form a smooth paste. This paste was used to apply coatings on the glass plates and alumina plates using the screen-printing method

An array of 8x10 circular spots of 1mm diameter was screen-printed with this paste on a glass plate of 1mm thickness. After drying at 60 °C for 20 minutes in an electric furnace, the temperature was raised at a rate of 5 degrees per minute to 560 °C where it was held for 20 minutes. After cooling to room temperature, a glass plate with 8x10 porous ceramic array on its surface was obtained.

Example 7

26g liquid ceramic carrier B1 was mixed with 40g Y_2O_3 (4%) stabilised zirconia (having particle sizes less than 1 microns to form a smooth paste. This paste was used to apply coatings on the glass plates.

An array of 8x10circular spots of 1mm diameter was screen-printed with this paste on a glass plate of 1mm thickness. After drying at 60 °C for 20 minutes in an electric furnace, the temperature was raised at a rate of 5 degrees per minute to 560 °C where it was held for 20 minutes. After cooling to room temperature, a glass plate with an array of 8x10 porous ceramic spots (the diameter of the spots was about 1mm) on its surface was obtained.

Example 8

56g liquid ceramic carrier B1 was mixed with 4g aluminium oxide powder having particle sizes less than 0.1 micron (Degussa aluminium oxide C) to form a smooth paste. This paste was used to apply coatings on the glass plates.

An array of 20x60 circular spots of 0.4mm diameter was screen-printed with this paste on a glass plate of 1mm thickness. After drying at 40 °C for 30 minutes in an electric furnace, the temperature was raised at a rate of 3 degrees per minute to 560 °C where it was held for 20 minutes. After cooling to room temperature, a glass plate with an array of 1200 porous ceramic spots on its surface was obtained.

Example 9

Same as Example 8 except that the plate on which the paste was screen-printed was a 1 mm thick alumina plate. Also the sintering of this arrayed plate was carried out at 800 °C for 30 minutes instead of 560 °C for 20 minutes.

Example 10

54g liquid ceramic carrier B1 was mixed with 4g aluminium oxide powder having particle sizes less than 0.1 micron (Degussa aluminium oxide C) and 20g alumina powder having particle sizes between 0 – 0.5 microns to form a smooth paste

An array of 20x60 circular spots of 0.4mm diameter was screen-printed with this paste on a glass plate of 1mm thickness. After drying at 40 °C for 30 minutes in an electric furnace, the temperature was raised at a rate of 3 degrees per minute to 560 °C where it was held for 20 minutes. After cooling to room temperature, a glass plate with an array of 1200 porous ceramic spots on its surface was obtained.

Example 11

52g liquid ceramic carrier B2 was mixed with 50g titanium oxide powder having particle sizes less than 0.1 micron to produce a smooth paste. This paste was used to coat the whole surface of a normal 25mmx76mmx1mm glass slide by means of doctor blade. Thus coated glass slide was dried at 50 °C for 30 minutes in a furnace. Next the furnace temperature was raised at a rate of 3 degrees per minute to 550 °C. Once the temperature reached 550 °C, the furnace was switched off to cool to room temperature naturally in the furnace. The resultant product was a glass slide of which one surface was covered with a pervious layer of porous ceramic containing mainly TiO_2 .

Example 12

Same as Example 11 except that the plate on which the porous ceramic was coated was a 25mmx76mmx1mm alumina plate.

Example 13

Same as Example 11 except that the paste with which the glass plate was coated was prepared with 50g liquid ceramic carrier B2 and 70g aluminium oxide having particle sizes less than 0.5 micron.

Example 14

55g liquid ceramic carrier C1 was mixed with 2g fumed silica (AEROSIL[®] MOX 170) and 12g silica powder having particle size less than 0.5 micron to form a smooth paste. This paste was used to apply coatings on the glass plates.

An array of 20x60 circular spots of 0.4mm diameter was screen-printed with this paste on a glass plate of 1mm thickness. After drying at 50 °C for 30 minutes in an electric furnace, the temperature was raised at a rate of 3 degrees per minute to 550 °C where it was held for 20 minutes. After cooling to room temperature, a glass substrate with an array of 1200 porous ceramic spots on its surface was obtained.

Example 15

28.5g liquid ceramic carrier C1 was mixed with 5g titanium oxide powder (particle sizes smaller than 0.1 micron, Degussa P25) and 10g titanium oxide powder having particle sizes less than 1 micron to form a smooth paste.

An array 8x10 of circular spots of 1mm diameter was screen-printed with this paste on a glass plate of 1mm thickness. After drying at 50 °C for 30 minutes it was fired at 550 for 30 minutes. After cooling to room temperature, a glass plate with an 8x10 porous ceramic array attached to its surface was obtained.

Example 16

Same as example 15 except that the paste with which the glass plate was screen-printed was prepared with 50g liquid ceramic carrier C1 and 72g Y_2O_3 (5%) stabilised zirconium oxide powder having particle sizes less than 1 micron.

Example 17

Same as example 15 except that the paste with which the glass plate was screen-printed was prepared with 50g liquid ceramic carrier C1 and 50g Zinc oxide powder having particle sizes less than 1 micron. The drying was performed at 60 °C for 30 minutes and sintering at 500 °C for 20 minutes.

Example 18

Same as example 15 except that the paste with which the glass plate was screen-printed was prepared with 55g liquid ceramic carrier C1 and 75g barium titanate ($BaTiO_3$) powder having particle size less than 1 micron. The drying was performed at 60 °C for 30 minutes and sintering at 550 °C for 20 minutes.

Example 19

This example is described with reference to Figure 3

84g liquid ceramic carrier A1 was mixed with 4g fumed silica powder (Degussa) having particle sizes less than 0.1 micron and 20g silica (amorphous silica powder, particle sizes less than 0.5 micron) to produce a thin but smooth paste (or a wet ceramic as may be referred to as in other examples).

A surface of a 25mmx50mmx1mm glass base plate was coated with a positive Photoresist Sp2029 (Shipley Inc, UK). The coated surface was then exposed to ultra-violet radiation through a special mask with a pattern of 6x12 array of 1mmx1mm squared elements with the distance between each element being 1mm. Next this plate was immersed in a developing solution (sodium hydroxide solution) during which the exposed square elements of the coated Photoresist film was removed, whereas the frame surrounding the square elements made of Photoresist layer that had not undergone UV radiation remained on the surface of the glass plate (with reference to Figure 3B), this layer of frame would provide a mask to prevent a direct contact (or sticking) of porous ceramic to be coated in the next step with the glass base plate.

Next the overall surface of the above photolithographically patterned plate was coated by screen-printing or by doctor-blade method with the ceramic paste as described earlier in this example.

Next the coated plate was dried at 50 °C for 30 minutes and fired at 560 °C for 20 minutes. The temperature was raised at a rate of 5°C per minute and cooled at a rate of 10°C per minute. During the firing the photoresist frame (on which the wet ceramic paste was also

attached) was burned off, which resulted in detaching of the porous ceramic coating positioned on the top of it

The obtained sample was a glass plate with an array of 6x12 porous ceramic squares attached to a surface of it.

Example 20

The same method as described in Example 19 was used to prepare a glass substrate with an array of 6x12 porous ceramic squares attached to a surface of it in this example except that the coating ceramic paste was prepared by mixing of the following ingredients:

100g liquid ceramic carrier A2

6g aluminium oxide powder (particle sizes less than 0.1 micron, Degussa Al_2O_3 C)

20g aluminium oxide powder (particle sizes less than 0.5micron).

This example is given with reference to Figure 3.

Example 21

In this example, the same method as described in Example 19 was used to prepare a glass plate with an array of 6x12 porous ceramic squares attached to a surface of it except that the wet coating ceramic was prepared by mixing of following ingredients:

100g liquid ceramic carrier B2

12g Titanium oxide powder (particle sizes less than 0.1 micron, Degussa p25 TiO_2)

20g Titanium oxide powder (particle sizes less than 1 micron)

This example is given with reference to Figure 3.

Example 22

In this example, the same method as described in Example 19 was used to prepare a glass plate with an array of 12x36 circular porous ceramic spots having diameter of 0.5 mm attached to a surface of it except that the wet coating ceramic was prepared by mixing of following ingredients:

50g liquid ceramic carrier C1

24g zirconium oxide powder having particle size less than 0.5 micron.

This example is given with reference to Figure 3.

Example 23

In this example, the same method as described in Example 19 was used to prepare a glass plate with an array of 12x36 circular porous ceramic spots having diameter of 0.5 mm attached to a surface of it except that the coating wet ceramic was prepared by mixing of the following ingredients:

50g liquid ceramic carrier C1

30g Y_2O_3 stabilised ZrO_2 powder having particle size less than 1 micron.

This example is given with reference to Figure 3.

Example 24

In this example, the same method as described in Example 19 was used to prepare a glass plate with an array of 12x36 circular porous ceramic spots having diameter of 0.5 mm attached to a surface of it except that the wet coating ceramic was prepared by mixing of the following ingredients:

50g liquid ceramic carrier C2

4g silica powder having particle sizes less than 0.1 micron. (Degussa fumed silica powder)

This example is given with reference to Figure 3

Example 25

In this example, the same method as described in Example 19 was used to prepare a glass plate with an array of 12x36 circular porous ceramic spots having diameter of 0.5 mm attached to a surface of it except that the coating ceramic paste was prepared by mixing of following ingredients:

50g liquid ceramic carrier C2

4g silica powder having particle sizes less than 0.1 micron. (Degussa fumed silica powder)

10g amorphous silica powder having particle sizes less than 0.5 micron

This example is given with reference to Figure 3.

Example 26

This example is described with reference to Figure 2.

A 1mm thick impervious alumina plate was machined to have a 4x12 array of through holes. The diameter of the said through holes was 0.3mm. The distance between the holes was 1mm. These holes were used to contain a microporous ceramic medium.

The wet ceramic paste was prepared by mixing following ingredients:

32g liquid ceramic carrier A1

4g silica powder having particle sizes less than 0.1 micron. (Degussa fumed silica powder)

20g amorphous silica powder having particle sizes less than 0.5 micron

A small amount of the as prepared ceramic paste was placed onto the above said alumina plate and the paste was scraped with a soft robber blade across the area where the array of through holes were positioned. This operation forced the wet ceramic paste to fill holes in the plate (this operation may be repeated until all the holes are filled with the paste). Next the surplus of the paste on both sides of the alumina plate were wiped and cleaned with a piece of soft tissue (or soft cloth).

Next the wet ceramic filled plate was dried in a furnace at 60 °C for 30 minutes and then temperature was raised to 750 °C where it was held for 10 minutes for the filled porous ceramic to be sintered.

After cooling down to room temperature at a rate of 5-10 degree per minute, an alumina plate with an array of 48 three-dimensional porous ceramic spots embedded in it was obtained. Such a plate allows 48 different chemical species to be isolated or immobilised in it.

Example 27

This example is described with reference to Figure 2.

An impervious 6mmx12mmx0.5mm alumina plate was machined to have a 6x12 array of through holes. The diameter of the said through holes was 0.15mm. The distance between the holes was 0.5mm. These holes were used to contain a microporous ceramic medium.

The wet ceramic paste was prepared by mixing following ingredients.

58g liquid ceramic carrier A2

1.2g Al_2O_3 powder having particle sizes less than 0.1 micron (Degussa Al_2O_3 C)

5.2g Al_2O_3 powder having particle sizes less than 0.5 micron

A small amount of the as prepared ceramic paste was placed onto the above said alumina plate and the paste was scraped with a soft robber blade across the area where the array of through holes were positioned. This operation forced the wet ceramic paste to fill holes in the plate (this operation may be repeated until all the holes are filled with the paste). Next the

surplus of the paste on both sides of the alumina plate were wiped and cleaned with a piece of soft tissue (or soft cloth).

Next the filled plate was dried in a furnace at 50 °C for 30 minutes and then temperature was raised to 700 °C where it was held for 10 minutes for the filled porous ceramic to be sintered.

After cooling down to room temperature at a rate of 5-10 degree per minute, a 6mmx12mmx0.5mm alumina plate with an array of 72 three-dimensional porous ceramic spots embedded in it was obtained. Such a plate allows 72 different chemical species to be isolated or immobilised in it.

Example 28

In this example, the same method as described in Example 27 was used to prepare an alumina plate with an array of 6x12 three-dimensional porous ceramic spots embedded in it except that the wet ceramic paste was prepared by mixing of the following ingredients:

40g liquid ceramic carrier B2

16g Titanium oxide powder having particle sizes less than 0.1 micron. (Degussa P25 TiO₂)

This example is given with reference to Figure 2.

Example 29

In this example, the same method as described in Example 27 was used to prepare an alumina plate with an array of 6x12 three-dimensional porous ceramic spots embedded in it except that the wet ceramic paste was prepared by mixing of the following ingredients:

40g liquid ceramic carrier B2

16g Titanium oxide powder having particle sizes less than 0.1 micron. (Degussa P25 TiO₂)

10g Titanium oxide powder having particle sizes less than 1 micron.

This example is given with reference to Figure 2.

Example 30

In this example, the same method as described in Example 27 was used to prepare an alumina plate with an array of 6x12 three-dimensional porous ceramic spots embedded in it except that the wet ceramic paste was prepared by mixing of the following ingredients:

40g liquid ceramic carrier B2

5g silica powder having particle sizes less than 0.1 micron. (Degussa fumed silica powder)

30g amorphous silica powder having particle sizes less than 0.5 micron

This example is given with reference to Figure 2.

Example 31

In this example, the same method as described in Example 27 was used to prepare an alumina plate with an array of 6x12 three-dimensional porous ceramic spots embedded in it except that the wet ceramic paste was prepared by mixing of the following ingredients:

48g liquid ceramic carrier C1

20g Al₂O₃ powder having particle sizes less than 0.1 micron (Degussa Al₂O₃ C)

16g amorphous silica powder having particle sizes less than 0.5 micron

This example is given with reference to Figure 2.

Example 32

In this example, the same method as described in Example 27 was used to prepare an alumina plate with an array of 6x12 three-dimensional porous ceramic spots embedded in it except that the wet ceramic paste was prepared by mixing of the following ingredients:

)
52g liquid ceramic carrier C2

43g Titanium oxide powder having particle sizes less than 0.1 micron. (Degussa P25 TiO₂)

This example is given with reference to Figure 2.

Example 33

In this example, the same method as described in Example 27 was used to prepare an alumina plate with an array of 6x12 three-dimensional porous ceramic spots embedded in it except that the wet ceramic paste was prepared by mixing of the following ingredients:

52g liquid ceramic carrier C2

42g Titanium oxide powder having particle sizes less than 0.1 micron. (Degussa P25 TiO₂)

20g Titanium oxide powder having particle sizes less than 1 micron

This example is given with reference to Figure 2.

CLAIMS

1. A method of making a substrate consisting of a base plate and a porous ceramic pattern attached to a surface of such a base plate, in which the pattern is screen-printed on the base plate with a specially formulated wet ceramic paste, thereafter the screen-printed plate is dried and sintered at elevated temperatures to convert the wet ceramic pattern into a pervious ceramic pattern, substantially as herein described with reference to Figure 1.
2. A method of making a substrate consisting of a base plate and an array of porous ceramic medium embedded in the through holes in the base plate, wherein the through holes are first machined in the base plate and then they are filled with a specially formulated wet ceramic paste, thereafter the wet ceramic filled substrate is dried and sintered at elevated temperatures, substantially as herein described with reference to Figure 2.
3. An impervious ceramic or glass substrate containing an array of through holes that are filled with a porous ceramic medium, as manufactured with the method herein described in Claim 2, substantially as herein described with reference to Figure 2.
4. A combined method, substantially as herein described with reference to Figure 3, of photolithographic patterning and wet ceramic coating to make a substrate consisting of a base plate and a pattern of porous ceramic attached to a surface of such a base plate, wherein the combined method comprises the steps of photolithographic patterning of the base plate surface, coating the patterned surface with a wet ceramic paste or a ceramic suspension and sintering of thus coated plate at a elevated temperature, wherein the photolithographic patterning comprises the steps of coating the base plate with a positive photoresist film, exposing thus coated surface to UV radiation through a special mask with a required pattern and leaching off the exposed parts or sections by immersing the radiated plate in a developing solution.
5. A method according to Claims 1, 2, 3 and 4, wherein the base plate is a glass plate or an impervious ceramic plate (e.g. 1mm thick alumina plate).
6. A method according to Claims 1, 2, 3 and 4, wherein the wet ceramic paste or ceramic suspension is prepared by mixing one or more metal oxide powders as herein given in Table I with a liquid ceramic carrier having a composition within the range:
 $(C_2H_5)_4Si$ (Tetraethyl Silicate): 10-50% by weight
 Methanol or/and ethanol: 20-70% by weight
 10% H_3PO_4 aqueous solution: 0-10% by weight
 10% HCl or/and 10% HNO_3 aqueous solution. 0-10% by weight
 The balance (to 100% by weight) consists of only pure water.
7. A method according to Claims 1, 2, 3 and 4, wherein the wet ceramic paste or ceramic suspension is prepared by mixing one or more metal oxide powders as herein given in Table I with a liquid ceramic carrier having a composition within the range:
 Colloidal silica (e.g. Du Pont Syton X30, W30): 5% – 30% by weight
 Boric Oxide (B_2O_3): 0%-8% by weight
 10% H_3PO_4 aqueous solution 0.2-10% by weight
 The balance (if any) to 100% (by weight) consists of only water.

CLAIMS

8. A method according to Claims 1, 2, 3 and 4, wherein the wet ceramic paste or ceramic suspension is prepared by mixing one or more metal oxide powders as herein given in Table I with a liquid ceramic carrier having a composition within the range:
Zirconyl Chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$): 2.5-40% by weight
Colloidal silica (e.g. Syton X30, W30, and W50): 0-15% by weight
The balance to 100% (by weight) consists of only water.
9. A method according to Claims 1, 2, 3 and 4, wherein the sintering temperatures for glass substrates having patterns of porous ceramics attached to a surface thereof or embedded in the through holes thereof are in the range of 250-560°C.
10. A method according to Claims 1, 2, 3 and 4, wherein the sintering temperatures for impervious ceramic substrates having patterns of porous ceramics attached to a surface thereof or embedded in the through holes thereof are in the range of 500-1000°C.
11. A method according to Claims 1, 2 and 4, wherein the patterns of porous ceramics includes arrays of spots of circular shape, rectangular shapes, and patterns that are obtainable by screen-printing and photolithography.
12. A method according to Claims 1 and 3, wherein the shapes of through holes are circular, square and rectangular.



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Application No: GB 0308032.2
Claims searched: 1, 5-12

17

Examiner: Michael Young
Date of search: 24 September 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

| Category | Relevant to claims | Identity of document and passage or figure of particular relevance |
|----------|--------------------|--|
| A | | WPI A.A.N: 2002-576265 [62] & DE 10059328 A1 (SIEMENS) (11/7/02). |

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